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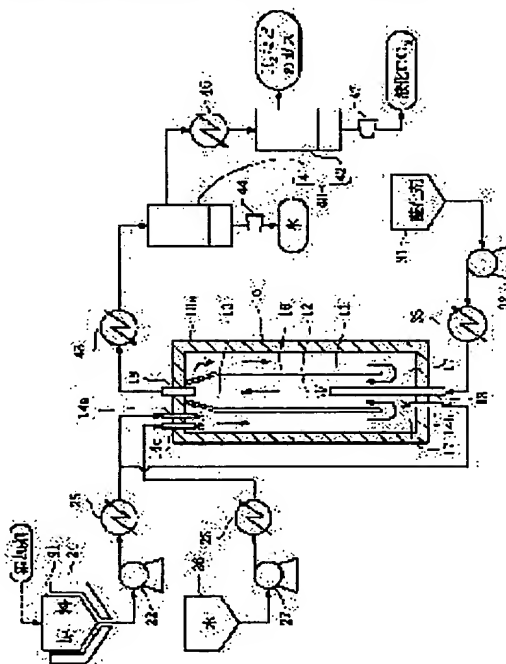
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(54) PRODUCTION OF HYDROGEN GAS AND THE LIKE AND APPARATUS THEREFOR

(57)Abstract:

PROBLEM TO BE SOLVED: To produce a hydrogen gas of high purity without necessitating a complicated process and to recover by-produced liquefied carbon dioxide of high purity.

SOLUTION: Carbon resources are reacted with a subcritical or supercritical water at 300–650° C and 7–35 MPa in the region 11 of a reactor 10 to effect thermolysis and hydrolysis of the carbon resources to give lightened gases, oils and residue. The abovementioned gases, oils and residue are reacted with a subcritical or supercritical water at 650–1,200° C and 7–35 MPa in the region 12 to form a gas composed mainly of hydrogen, carbon dioxide, carbon monoxide and methane. The gas is converted into a gas composed mainly of hydrogen and carbon dioxide at 450–1,000° C and 7–35 MPa in the region 13. The combustion of a part of the gases, the oil components and the residue by adding an oxidizing agent in the region 12 supplies necessary heat for the regions 11 and 12 and cools the region 13 by heat exchange with the region 11 and endothermic reactions.



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CLAIMS

[Claim(s)]

[Claim 1] In the 1st reaction field (11) of a reactor (10) The temperature of 300–650 degrees C, The gas ***** (ed) by making the carbon resource which is a raw material in pressure 7–35MPa react with subcritical or supercritical water, and performing either or the both sides of the pyrolysis of said carbon resource, or hydrolysis, Oil and residue are generated and it sets to the 2nd reaction field (12) of said reactor (10). The temperature of 650–1200 degrees C, By making said ***** (ed) gas, oil, and residue react with subcritical or supercritical water, and ***** (ing) and gasifying them further by pressure 7–35MPa The gas which uses hydrogen, a carbon dioxide, a carbon monoxide, and methane as a principal component is generated. In the 3rd reaction field (13) of said reactor (10) The temperature of 450–1000 degrees C, They are the manufacture approaches, such as hydrogen gas which converts said gas into the gas which uses hydrogen and a carbon dioxide as a principal component by pressure 7–35MPa. An oxidizer is added to said 2nd reaction field (12). Gas, oil, The manufacture approaches, such as hydrogen gas characterized by said 3rd reaction field (13) being cooled by the heat exchange and endothermic reaction to said 1st reaction field (11) while filling up heat required for said 1st and 2nd reaction field (11 12) by burning a part of residue.

[Claim 2] The manufacture approaches, such as hydrogen gas according to claim 1 which adds an additive in at least one field among the 1st reaction field (11) of a reactor (10), the 2nd reaction field (12), or the 3rd reaction field (13).

[Claim 3] The manufacture approaches, such as hydrogen gas according to claim 1 which collects carbon dioxides in the state of the liquid of a high grade by setting to the temperature of –20–31 degrees C, and pressure 2–35MPa the gas which uses as a principal component the hydrogen and the carbon dioxide which were converted in the 3rd reaction field (13).

[Claim 4] The 1st reaction field where both ends were established in the inner circumference section of the reactor (10) of the shape of tubing by which the closure was carried out (11), The 2nd reaction field established in the core of said reactor (10) (12), The 3rd reaction field established in the core of said reactor (10) following said 2nd reaction field (12) (13), Each pressure of said 1st, 2nd, and 3rd reaction field is maintained to 7–35MPa. The temperature of said 1st, 2nd, and 3rd reaction field, respectively 300–650 degrees C, It has a means (22, 27, 32, 25, 28, 33, 16) to maintain at 650–1200 degrees C and 450–1000 degrees C. The feed hopper (14a, 14b, 14c) of the carbon resource which leads to said 1st reaction field (11), and water is prepared for either or the both sides of the end of said reactor (10), or the other end. It is divided with the heat-resistant dashboard (16) with which said 1st reaction field (11) and said 2nd reaction field (12) consist of a tubed thermal conductor. It has the free passage section (17) which opens said 1st reaction field (11) and said 2nd reaction field (12) for free passage to the other end side of the reactor of said dashboard (16). Manufacturing installations, such as hydrogen gas characterized by having prepared the delivery pipe (18) which supplies an oxidizer in said 2nd reaction field (12) at the other end of said reactor (10), and preparing the exhaust port (19) of the gas which uses hydrogen and a carbon dioxide as a principal component at the end of said reactor (10).

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DETAILED DESCRIPTION

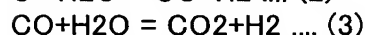
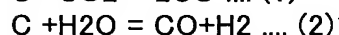
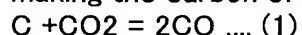
[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the approach of manufacturing pure hydrogen gas, from heavy resources, such as heavy oil and coal, or the carbon resource which pyrolyzed this heavy resource.

[0002]

[Description of the Prior Art] The reaction is shown by following reaction-formula (1) – (3), when making the carbon of a carbon resource react with a steam and gasifying it generally.



In the above-mentioned formula (1) and (2), since a reaction is endothermic reaction, carbonaceous is completely gasified by promoting a reaction and using a catalyst if needed by heating at the elevated temperature which is 800–1800 degrees C.

[0003]

[Problem(s) to be Solved by the Invention] However, since the water gas shift reaction based on a formula (3) does not fully advance when manufacturing hydrogen gas by the reaction of above-mentioned formula (1) – (3) by the gasifier, unreacted carbon monoxide gas remains in a product. Therefore, the shift converter which used the expensive catalyst needs to advance the reaction of through and a formula (3). Moreover, since several % – about ten% of ash content, a metal impurity, sulfur, nitrogen, etc. are contained in the carbon resource of a raw material, in order to remove these, it is necessary to refine a product. Moreover, in pyrogenetic reaction, it is blockaded by the corks which the caulking phenomenon produced and some reactors produced at the reaction, and there is un-arranging — an expensive heat-resisting material is needed for a reactor. Furthermore, since the choke damp which is a by-product is difficult to collect, it is emitted into atmospheric air and has an environment top problem.

[0004] The purpose of this invention is to offer the approach and equipment which manufacture the hydrogen gas of a high grade, without requiring a complicated process. Another purpose of this invention is to offer the approach and equipment which collect the liquefaction carbon dioxides of a high grade as a by-product.

[0005]

[Means for Solving the Problem] Invention concerning claim 1 is set to the 1st reaction field 11 of a reactor 10, as shown in drawing 1 . The temperature of 300–650 degrees C, The gas ***** (ed) by making a carbon resource react with subcritical or supercritical water by pressure 7–35MPa, and performing either or the both sides of the pyrolysis of this carbon resource, or hydrolysis, Oil and residue are generated and it sets to the 2nd reaction field 12 of a reactor 10. The temperature of 650–1200 degrees C, By making the gas, oil, and residue by which ***** was carried out [above-mentioned] react with subcritical or supercritical water, and ***** (ing) and gasifying them further by pressure 7–35MPa The gas which uses hydrogen, a carbon dioxide, a carbon monoxide, and methane as a principal component is generated. They are the manufacture approaches, such as hydrogen gas which converts the above-mentioned gas into

the gas which uses hydrogen and a carbon dioxide as a principal component in the 3rd reaction field 13 of a reactor 10 by the temperature of 450–1000 degrees C, and pressure 7–35MPa. An oxidizer is added to the 2nd reaction field 12. Gas, oil, While filling up heat required for the above-mentioned 1st, 2nd, and 3rd reaction field by burning a part of residue, they are the manufacture approaches, such as hydrogen gas characterized by the 3rd reaction field being cooled by the heat exchange and endothermic reaction to the 1st reaction field. Since subcritical [high-pressure] or the water of a supercritical condition has high fluid density, it contacts efficiently to the carbon particle of the carbon resource which exists in the system of reaction, and the active species of a reaction process. Therefore, the hydrogen gas of a high grade and the carbon dioxide of a high grade are efficiently manufactured by setting up the generation condition of hydrogen gas and a carbon dioxide the optimal. heat required for advance of the reaction of the 1st and 2nd reaction field boils a part of gas, oil, and residue with the heat of combustion when burning with an oxidizer, and is filled up. Moreover, the heat of the 3rd reaction field is consumed by the temperature up of the 1st reaction field, and since the reaction of the 3rd reaction field is endothermic reaction, the temperature of the 3rd reaction field falls from the temperature of the 2nd reaction field.

[0006] Invention concerning claim 2 is invention concerning claim 1, and is the manufacture approaches, such as hydrogen gas which adds an additive in at least one field among the 1st reaction field 11 of a reactor 10, the 2nd reaction field 12, or the 3rd reaction field 13. If the additive which consists of the oxide of alkali metal or alkaline earth metal, a hydroxide, a carbonate, etc. is added, the water gas-ized reaction of the above-mentioned formula (2) and the water gas shift reaction of the above-mentioned formula (3) will be performed more efficiently, and more gas which uses hydrogen gas and the choke damp as a principal component will be generated.

[0007] Invention concerning claim 3 is invention concerning claim 1, and is the manufacture approaches, such as hydrogen gas which collects carbon dioxides in the state of the liquid of a high grade, by setting to the temperature of –20–31 degrees C, and pressure 2–35MPa the gas which uses as a principal component the hydrogen and the carbon dioxide which were converted in the 3rd reaction field 13. By operating temperature and a pressure for the gas which uses as a principal component the hydrogen and the carbon dioxide which were converted in the 3rd reaction field 13, phase separation of hydrogen and the carbon dioxide is carried out. While leading to warming prevention of earth environment by collecting carbon dioxides in the state of a liquid, without emitting into atmospheric air, the recycle to a chemistry raw material etc. is attained.

[0008] The 1st reaction field 11 where both ends were established in the inner circumference section of the reactor 10 of the shape of tubing by which the closure was carried out as invention concerning claim 4 was shown in drawing 1 , The 2nd reaction field 12 established in the core of a reactor 10, and the 3rd reaction field 13 established in the core of a reactor 10 following the 2nd reaction field 12, Each pressure of the 1st, 2nd, and 3rd fields of the above is maintained to 7–35MPa. The temperature of the above-mentioned 1st, 2nd, and 3rd reaction field, respectively 300–650 degrees C, It has means 22, 27, 32, 25, 28, 33, and 16 to maintain at 650–1200 degrees C and 450–1000 degrees C. The feed hoppers 14a, 14b, and 14c of the carbon resource which leads to the 1st reaction field 11, and water are prepared for either or the both sides of the end of a reactor 10, or the other end. It is divided with the heat-resistant dashboard 16 with which the 1st reaction field 11 and the 2nd reaction field 12 consist of a tubed thermal conductor. It has the free passage section 17 which opens the 1st reaction field 11 and the 2nd reaction field 12 for free passage to the other end side of the reactor 10 of a dashboard 16. They are manufacturing installations, such as hydrogen gas characterized by having formed the delivery pipe 18 which supplies an oxidizer in the 2nd reaction field 12 at the other end of a reactor 10, and forming the exhaust port 19 of the gas which uses hydrogen and a carbon dioxide as a principal component at the end of a reactor 10.

[0009] The water gas shift reaction of CO gas by endothermic reaction is made to perform in the reaction field 13 at the same time it adds an oxidizer, it makes the 2nd reaction field 12 into an elevated temperature and it makes a request react. The raw material of the 1st reaction field to

which the heat of the surplus produced in the reaction field 13 is supplied from the outside through a dashboard 16 etc. is made to absorb, and, thereby, the pyrolysis and hydrolysis reaction of a raw material are made to perform. Therefore, if combustion takes place in the 2nd reaction field 12, this heat serves as a heat source of the 1st reaction field 11, and supply of the heat energy from the reactor outside can be reduced. Moreover, in order that the low-temperature 1st reaction field 11 may surround the hot 2nd and 3rd reaction fields 12 and 13 through a dashboard, the thermal load of the peripheral wall of a reactor 10 is mitigated, and the range which selects the peripheral wall ingredient of a reactor is expanded. In this specification, "the supercritical condition of water" or "supercritical water" means the condition of the water which is in the pressure of 22 or more MPas at the temperature of 374 degrees C or more.

[0010]

[Embodiment of the Invention] The natural resource containing carbon, such as heavy oil (a crude oil, fuel oil A, B fuel oil, C fuel oil, atmospheric-distillation residue, vacuum distillation residue, bitumen, etc.), super-heavy oil, coal (grass peat, brown coal, subbituminous coal, bituminous coal, etc.), petroleum coke, coal corks, a pyrolysis char, plastics, rubber, natural gas, petroleum gas, and methane hydrate, scrap wood, trash, etc. are mentioned to the carbon resource used as a raw material by this invention. Although oil is not generated about gas, such as natural gas, manufacture of the hydrogen gas by the same processing as other solid-states thru/or a liquid-like carbon resource is possible. Moreover, oxygen, air, or a hydrogen peroxide is mentioned to the oxidizer of this invention. Furthermore, the oxide of alkaline earth metal, such as an oxide of alkali metal, such as a potassium and sodium, a hydroxide, a carbonate, etc. and magnesium, calcium, a hydroxide, a carbonate, etc. are mentioned to the additive of this invention.

[0011] In this invention, as shown in drawing 1, a raw material is processed in the single reactor 10 which has three reaction fields 11, 12, and 13 where it is pressure 7-35MPa, respectively, and temperature differs. This reactor 10 is formed in the shape of [to which the closure of the both ends was carried out] tubing. The 1st reaction field 11 is established for heater 10a for incubation in the inner circumference section again at the periphery section of a reactor 10, respectively. Moreover, the 2nd reaction field 12 is established in the core of a reactor 10, and the 3rd reaction field 13 is established in the core of a reactor 10 following this 2nd reaction field 12. Feed hopper 14a of the carbon resource which leads to the 1st reaction field 11, and feed hopper 14c of water are prepared in the end of a reactor 10, respectively, and feed hopper 14b of the carbon resource which leads to the 1st reaction field 11 is prepared in the other end of a reactor 10. The 1st reaction field 11 and the 2nd reaction field 12 are divided with the dashboard 16 of the heat-resistant metal which consists of a tubed thermal conductor, for example, the heat-resistant alloy of nickel-Cr, (trade name: MC alloy, MITSUBISHI MATERIALS make). A dashboard 16 is stuck to the wall of the end of a reactor 10, opens spacing with the wall of the other end of a reactor 10, and is formed. This spacing constitutes the free passage section 17 which opens the 1st reaction field 11 and the 2nd reaction field 12 for free passage, and the fluid which received the pyrolysis etc. flows into the reaction field 12 from this part. This dashboard 16 is exposed to an elevated temperature, and since there is a possibility that corrosion may become large, a dashboard 16 is constituted exchangeable. Furthermore, the delivery pipe 18 of an oxidizer penetrates in the core of the other end of a reactor 11, and it is extended and prepared to the 2nd reaction field 12 which went into the interior of a dashboard slightly from the edge of a dashboard 16. The exhaust port 19 which discharges the fluid which becomes the end of a reactor 10 from the hydrogen, the carbon dioxide and subcritical water, or supercritical water converted in the 3rd reaction field 13 is formed. Although drawing 1 showed the reactor 10 which has the single dashboard 16, the number of dashboards may surround the 2nd and 3rd reaction field with three-fold dashboards 16a, 16b, and 16c, as shown not only in this but in drawing 3. Five-fold [4-fold / a duplex and / and] are sufficient as this dashboard. The number of envelopment of this dashboard fully lowers the outer wall temperature of a reactor 10, and sets up only a number required to fully carry out the pyrolysis of the raw material. That is, the number of envelopment of this dashboard is determined from the thermal conductivity of a dashboard etc. in the ease of decomposing of the rate of heat recovery, and a

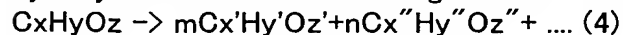
raw material. Moreover, although drawing 1 and drawing 3 show the reactor 10 which has the exhaust port 19 of the gas which carried out decomposition generation in the upper part, and has the delivery pipe 18 of an oxidizer in the lower part, not only this direction but an exhaust port may be made as the lower part, and it may make a delivery pipe the upper part, or the installation direction of a reactor installs a reactor horizontally, and you may make it arrange an exhaust port and a delivery pipe on right-and-left both sides.

[0012] The liquefied raw material stored in the tank 21 is fed with a pump 22 by the feed hoppers 14a and 14b of a carbon resource, and is supplied to them through a preheater 25. A heater 24 is formed in the perimeter of a tank 21, and a raw material is heated at 100–200 degrees C. The water stored in the tank 26 is fed with a pump 27 by feed hopper 14c of water, and is heated and supplied to it with a preheater 28 at 200–400 degrees C. Hydrogen peroxide solution of 50 – 60% of concentration which is the oxidizer stored in the tank 31 is fed with a pump 32 by the delivery pipe 18, and is heated and supplied to it with a preheater 33 at 200–600 degrees C. It is desirable that the additive which becomes a tank 21 from the oxide of alkali metal or alkaline earth metal, a hydroxide, a carbonate, etc. is added. The interior of a reactor 10 is maintained by 300–1200 degrees C by combustion in heater 10a and the 2nd reaction field 12 of pumps 22, 27, and 32, preheaters 25, 28, and 33, a dashboard 16, a heater 24, and a reactor 10. An eliminator 40 is connected to an exhaust port 19, and various gas is separated here. An eliminator 40 is constituted from the gestalt of this operation by the 1st eliminator 41 and the 2nd eliminator 42 which have a vapor–liquid–separation function, respectively. That is, a condensator 43, the 1st eliminator 41, and a reducing valve 44 are connected to an exhaust port 19. A condensator 46, the 2nd eliminator 42, and a reducing valve 47 are further connected to the 1st eliminator 41.

[0013] Next, the reaction by such equipment is explained.

(a) Introduce the carbon resource and water of reaction place ***** in the 1st reaction field into the 1st reaction field 11 of a reactor 10, and make them react in the state of subcritical [of the temperature of 300–650 degrees C, and the water of pressure 7–35MPa], or supercritical. This reaction is either or the both sides of the pyrolysis of a carbon resource, or hydrolysis, and the gas, oil, and residue which were ***** (ed) by this decomposition reaction are generated. The desirable reaction conditions of the 1st reaction field 11 are 380–500 degrees C, a pressure 10 – 30MPa extent, when a raw material is subbituminous coal, when a raw material is bituminous coal, they are 480–650 degrees C, a pressure 10 – 30MPa extent, and when a raw material is heavy oil, they are 400–600 degrees C, a pressure 10 – 30MPa extent. Since these conditions change with raw material classes, it is necessary to decide the optimal reaction condition according to the class of raw material. Less than 300 degrees C and a pressure have [the temperature of the 1st reaction field 11] a slow reaction rate in less than 7 MPas, and if the temperature of the 1st reaction field 11 exceeds 650 degrees C and a pressure exceeds 35MPa (s), a load is applied to a reactor 10 too much, and it is not efficient.

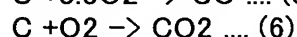
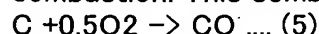
[0014] In order to give a fluidity on the occasion of the pyrolysis and hydrolysis of a carbon resource, when a carbon resource is a solid–state, a carbon resource is mixed with water and the 1st reaction field 11 is supplied with the gestalt of a slurry. A reaction is promoted by this and a caulking phenomenon is controlled. A carbon resource is ***** (ed) as a pyrolysis and hydrolysis show to the following reaction formula (4) in the 1st reaction field 11.



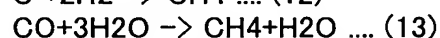
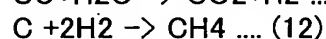
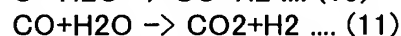
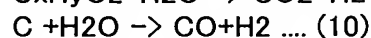
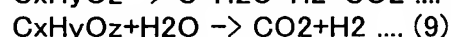
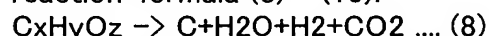
however -- x>x -- ' -- > -- x -- " -- y>y -- ' -- > -- y -- " -- z>z -- ' -- > -- z -- " -- it is -- m and n -- the number of arbitration -- it is . The hydrogen generation by cracking and the hydrogen generation by the gasification reaction of residue can also be made to perform in the 1st reaction field 11 by changing the temperature of the 1st reaction field to a 600–800–degree C elevated–temperature side in addition to making light ***** of the carbon resource of the above–mentioned formula (4) perform.

[0015] (b) The gas, oil, and residue which were generated in the 1st reaction field 11 of a reaction in the 2nd reaction field and which were ***** (ed) flow into the 2nd reaction field 12 through the free passage section 17. The hydrogen peroxide solution of an oxidizer is supplied to the 2nd reaction field 12 with a delivery pipe 18 here. To this oxidizer, the additive which

consists of the oxide of alkali metal or alkaline earth metal, a hydroxide, a carbonate, etc. may be added. A part of an oxidizer, gas which has flowed, oil, and residue burn, and the 2nd reaction field 12 becomes the elevated temperature which is 650–1200 degrees C with heat of combustion. This combustion reaction is shown by following formula (5) – (7).



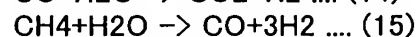
The reaction in the 2nd reaction fields 12 other than a combustion reaction is shown by following reaction-formula (8) – (13).



The gas, oil, and residue which were *****ed by the above-mentioned reaction are *****ed and gasified further, and the gas which uses hydrogen, a carbon dioxide, a carbon monoxide, and methane as a principal component is generated. The desirable temperature of the 2nd reaction field 12 is 700–1100 degrees C, and a desirable pressure is 10–30MPa.

[0016] (c) Convert the gas which uses as a principal component the hydrogen generated in the 2nd reaction field 12 of a reaction in the 3rd reaction field, a carbon dioxide, a carbon monoxide, and methane into the gas which uses hydrogen and a carbon dioxide as a principal component in the 3rd reaction field 13. The temperature of this 3rd reaction field 13 is 450–1000 degrees C, and a pressure is 7–35MPa. The desirable temperature of the 3rd reaction field 13 is 550–800 degrees C, and a desirable pressure is 10–30MPa. The reaction in the 3rd reaction field 13 is shown by following reaction-formula (14) – (15).

[0017]



In this invention, it is making into the key objective to manufacture the gas which uses hydrogen and a carbon dioxide as a principal component based on the conversion reaction in the above-mentioned 3rd reaction field 13. However, it is also possible to manufacture the gas which was rich in carbon monoxide gas or methane in addition to this based on above-mentioned reaction-formula (8) – (15) by combining reaction temperature, reaction pressure, an additive, etc. suitably. The block diagram when manufacturing hydrogen gas and a liquefaction carbon dioxide to drawing 2 (a) is shown. Although the hydrogen and the carbon dioxide which were generated serve as subcritical, or supercritical water and a homogeneity phase under elevated-temperature high pressure, if a pressure and temperature are lowered, hydrogen gas and a liquefaction carbon dioxide are separable according to an individual. The block diagram when manufacturing hydrogen gas, carbon monoxide gas, and a liquefaction carbon dioxide to drawing 2 (b) is shown. The block diagram when manufacturing hydrogen gas, methane, and a liquefaction carbon dioxide to drawing 2 (c) is shown. Drawing 2 (a) In – (c), the same sign as drawing 1 shows the same device as drawing 1.

[0018] How to separate each of these components from subcritical [of water] or a supercritical condition is explained. Water will be in subcritical or a supercritical condition by the temperature of the reactor 10 interior, and the pressure, and hydrogen, a carbon dioxide, a carbon monoxide, and methane will also be in a supercritical condition. Each supercritical point is shown in the next table 1.

[0019]

[Table 1]

ガスの成分	温度 (℃)	圧力 (MPa)
水	374	22.4
二酸化炭素	31	7.5
水素	-240	1.3
一酸化炭素	-140	3.5
メタン	- 82.7	4.7

[0020] If it is below the supercritical point of water and the temperature and the pressure containing water, a carbon dioxide, hydrogen, a carbon monoxide, and methane of mixed gas are carried out beyond the supercritical point of a carbon dioxide, only water will carry out as a liquid from a supercritical phase, and a consistency will carry out phase separation as water of about 1 g/cm³ so that more clearly than the above-mentioned table 1. Next, the pressure and temperature of supercritical fluid from which water was separated are controlled, and it carries out below at the supercritical point of a carbon dioxide beyond the supercritical point of hydrogen and methane. By cooling and decompressing to 5MPa extent at 20 degrees C preferably, a carbon dioxide is made to liquefy and phase separation is carried out. Methane, hydrogen, and a carbon monoxide are obtained by separating only a liquefaction carbon dioxide by the succeeding same approach as water separation. A desired component is separable by the above-mentioned actuation by any approach of of drawing 2 (a), (b), and (c). Since the solubility of other gas constituents to a liquefaction carbon dioxide is small, the high liquefaction carbon dioxide of purity is obtained.

[0021] It returns to drawing 1 and the gas which uses as a principal component the hydrogen and the carbon dioxide which were converted in the 3rd reaction field 13 is cooled from the exhaust port 19 of a reactor 10 to the temperature below the supercritical point of water with a condenser 43. It is made to separate into vapor-liquid within an eliminator 41, and the cooled gas extracts only the water of a liquid through a reducing valve 44. Thereby, only water is separated as a liquid. The remaining gas is made to divide into a liquid CO₂ and a gas within an eliminator 42, after being sent to a condenser 46 and cooled to 20 degrees C here. A gas is gas which uses hydrogen gas as a principal component, and the carbon dioxide of a liquid is extracted through a reducing valve 47.

[0022]

[Example] Next, the example of this invention is explained.

The sample 1 – the sample 6 were followed in manufacture of the gas which contains hydrogen and a carbon dioxide, using as a carbon resource what distilled <example 1> coal dryly at 800 degrees C among nitrogen-gas-atmosphere mind. In six kinds of samples, the pressure in a reactor was set to 25MPa(s), and the hydrogen peroxide of an oxidizer was supplied so that the temperature of the 2nd reaction field might become 650 degrees C, 800 degrees C, and 1000 degrees C. Moreover, since generation of heat of a heating value only by the oxidizer was inadequate, the reactor was heated from the outside. By the sample 2, the sample 4, and the sample 6, potassium carbonate was used as an additive. The unreacted object was accumulated into the reactor and collected these as residue. In the eliminator shown in drawing 1, the product obtained from the exhaust port of a reactor was condensed with the gas condenser which is not illustrated, without dissociating, and after it measured capacity with the flowmeter, it carried out temporary storage of the generation gas to the container. The gas stored in this container was sampled and the component was analyzed. The result is shown in Table 2. As for samples 1–6, it turned out that a lot of hydrogen gas and choke damp are obtained by each so that more clearly than Table 2. When especially an additive was added, the inclination for generation of a carbon monoxide and methane to be controlled was checked. Moreover, the same inclination was checked also when temperature of the 2nd reaction field was made into

1200-degree C conditions.

[0023]

[Table 2]

試料No	温 度-圧 力-触 媒	ガス成分（容積％）			
		H ₂	CO ₂	CO	CH ₄
試料1	650℃-25MPa	63	34	0	3
試料2	650℃-25MPa-K ₂ CO ₃	66	34	0	0
試料3	800℃-25MPa	52	37	3	9
試料4	800℃-25MPa-K ₂ CO ₃	65	34	0	1
試料5	1000℃-25MPa	51	26	8	15
試料6	1000℃-25MPa-K ₂ CO ₃	62	35	1	2

[0024] The sample 7 - the sample 12 were followed in manufacture of the gas which repeats the same approach as an example 1, and contains hydrogen and a carbon dioxide except having used <example 2> petroleum bottoms as a carbon resource. The result is shown in Table 3. As for the samples 7-12 of this invention, it turned out that a lot of hydrogen gas and choke damp are obtained by each so that more clearly than Table 3. When especially an additive was added, the inclination for a carbon monoxide to be controlled was checked. Moreover, the same inclination was checked also when temperature of the 2nd reaction field was made into 1200-degree C conditions.

[0025]

[Table 3]

試料No	温 度-圧 力-触 媒	ガス成分（容積％）			
		H ₂	CO ₂	CO	CH ₄
試料7	650℃-25MPa	45	25	0	30
試料8	650℃-25MPa-K ₂ CO ₃	61	23	0	16
試料9	800℃-25MPa	46	24	4	26
試料10	800℃-25MPa-K ₂ CO ₃	67	25	0	7
試料11	1000℃-25MPa	55	26	8	11
試料12	1000℃-25MPa-K ₂ CO ₃	66	30	1	3

[0026] Temperature of the 2nd reaction field of <an example 3> was made into 800 degrees C, and the sample 13 - the sample 20 were followed in manufacture of the gas which repeats the same approach as an example 1, and contains hydrogen and a carbon dioxide except having changed the class of additive. The result is shown in Table 4. As for samples 13-20, it turned out that a lot of hydrogen gas and choke damp are obtained by each so that more clearly than Table 4. When especially an additive was added, the inclination for generation of a carbon monoxide and methane to be controlled was checked. Moreover, the generation rate of gas showed the inclination for an alkali-metal salt to become larger than an alkaline earth salt.

[0027]

[Table 4]

試料No	温 度-圧 力-触 媒	ガス成分（容積％）			
		H ₂	CO ₂	CO	CH ₄
試料13	800℃-25MPa	52	37	3	9
試料14	800℃-25MPa-K ₂ CO ₃	65	34	0	1
試料15	800℃-25MPa-KOH	63	35	1	1
試料16	800℃-25MPa-Na ₂ CO ₃	65	35	1	1
試料17	800℃-25MPa-NaOH	65	34	1	2
試料18	800℃-25MPa-CaCO ₃	66	34	0	1
試料19	800℃-25MPa-Ca(OH) ₂	62	35	1	2
試料20	800℃-25MPa-MgCO ₃	62	34	1	3

[0028] The sample 21 - the sample 23 were followed in manufacture of the gas which repeats the same approach as an example 1, and contains hydrogen and a carbon dioxide except having set the pressure in a <example 4> reactor to 7, 10, and 25MPa, and having made temperature of the 2nd reaction field into 800 degrees C. The result is shown in Table 5. In addition, the additive is not added about a sample 21 - a sample 23. As for samples 21-23, it turned out that a lot of hydrogen gas and choke damp are obtained by each so that more clearly than Table 5.

[0029]

[Table 5]

試料No	温 度-圧 力-触 媒	ガス成分（容積％）			
		H ₂	CO ₂	CO	CH ₄
試料21	800℃-25MPa	52	37	3	9
試料22	800℃-10MPa	54	35	4	7
試料23	800℃-7MPa	55	35	4	6

[0030] The sample 24 - the sample 26 were followed in manufacture of the gas which repeats the same approach as an example 1, and contains hydrogen and a carbon dioxide except having used <example 5> polypropylene as a carbon resource. The result is shown in Table 6. In addition, the additive is not added about a sample 24 - a sample 26. As for the samples 24-26 of this invention, it turned out that a lot of hydrogen gas and choke damp are obtained by each so that more clearly than Table 6. Especially when the temperature of the 2nd reaction field was set up low, the carbon monoxide was controlled, and the inclination for many methane to be generated was checked.

[0031]

[Table 6]

試料No	温 度－圧 力－触 媒	ガス成分（容積％）			
		H ₂	CO ₂	CO	CH ₄
試料24	650℃－25MPa	58	32	0	10
試料25	800℃－25MPa	59	32	2	7
試料26	1000℃－25MPa	61	30	6	3

[0032]

[Effect of the Invention] As stated above, according to this invention, it sets to the 1st reaction field of a reactor. The temperature of 300–650 degrees C, The gas ***** (ed) by making a carbon resource react with subcritical or supercritical water, and decomposing primarily by pressure 7–35MPa, By generating oil and residue, making the temperature of 650–1200 degrees C, the gas by which ***** was carried out [above-mentioned] by pressure 7–35MPa, oil, and residue react with subcritical or supercritical water, and ***** (ing) and gasifying them further in the 2nd reaction field The gas which uses hydrogen, a carbon dioxide, a carbon monoxide, and methane as a principal component is generated. In the 3rd reaction field, the above-mentioned gas is converted into the gas which uses hydrogen and a carbon dioxide as a principal component by the temperature of 450–1000 degrees C, and pressure 7–35MPa. Without requiring a complicated process, since the 3rd reaction field was cooled by the heat exchange and endothermic reaction to the 1st reaction field while filling up heat required for the above-mentioned 1st and 2nd reaction field by adding an oxidizer to the 2nd reaction field and burning a part of gas, oil, and residue The hydrogen gas of a high grade can be manufactured. Moreover, the liquefaction carbon dioxide of a high grade is recoverable as a by-product with an eliminator using the difference in a supercritical point.

[Translation done.]

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2.**** shows the word which can not be translated.

3.In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] The block diagram of manufacturing installations, such as hydrogen gas of this invention.

[Drawing 2] The block diagram showing the hydrogen gas of this invention, and manufacture of a carbon dioxide and others.

[Drawing 3] The block diagram of another reactor of this invention.

[Description of Notations]

10 Reactor

11 1st Reaction Field

12 2nd Reaction Field

13 3rd Reaction Field

14a, 14b Feed hopper of a carbon resource

14c The feed hopper of water

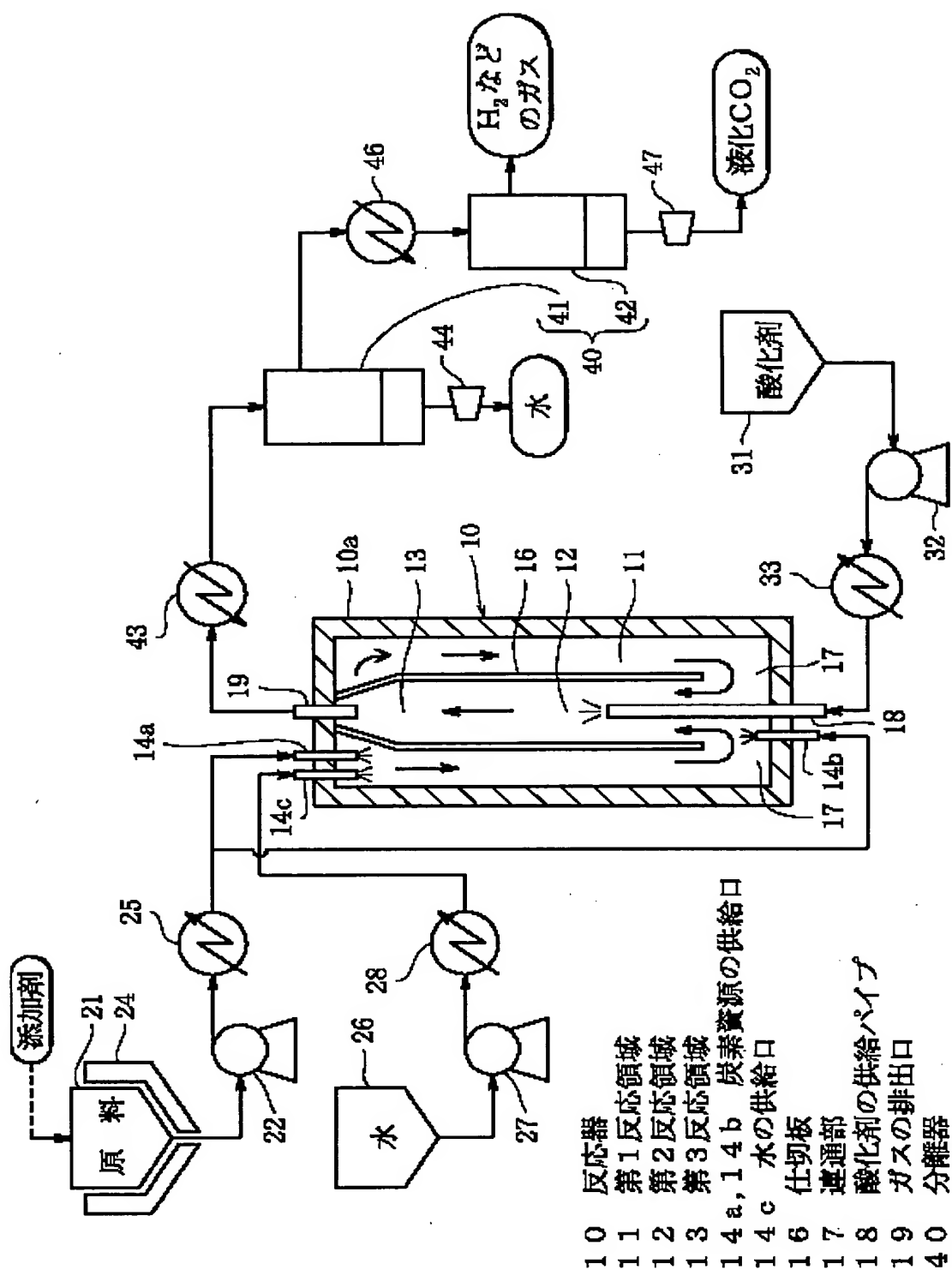
16 Dashboard

17 Free Passage Section

18 Delivery Pipe of Oxidizer

19 Exhaust Port of Gas

[Translation done.]



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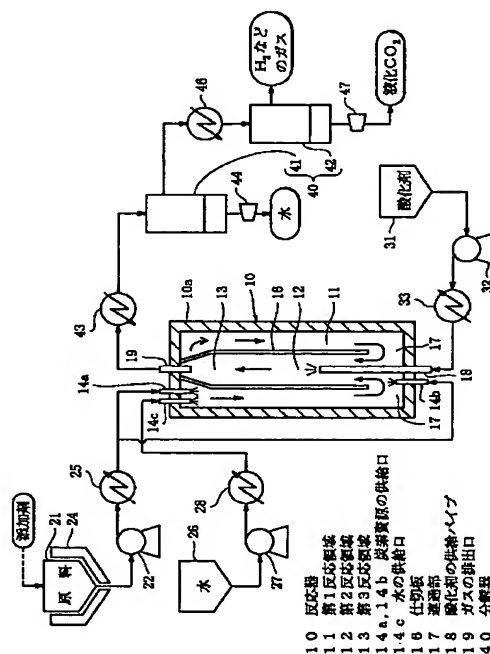
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(54) 【発明の名称】 水素ガス等の製造方法及びその装置

(57) 【要約】

【課題】 複雑なプロセスを要することなく、高純度の水素ガスを製造する。副生物である高純度の液化二酸化炭素を回収する。

【解決手段】 反応器10の領域11にて300~650℃、7~35MPaで炭素資源を亜臨界或いは超臨界水と反応させて炭素資源の熱分解と加水分解により軽質化されたガス、油分及び残渣を生成する。領域12にて650~1200℃、7~35MPaで上記ガス、油分及び残渣を亜臨界或いは超臨界水と反応させて水素、二酸化炭素、一酸化炭素及びメタンを主成分とするガスを生成する。領域13にて450~1000℃、7~35MPaで上記ガスを水素及び二酸化炭素を主成分とするガスに転換する。領域12に酸化剤を添加してガス、油分、残渣の一部を燃焼させることにより領域11、12に必要な熱を補充するとともに領域13が領域11への熱交換及び吸熱反応により冷却される。



【特許請求の範囲】

【請求項 1】 反応器(10)の第 1 反応領域(11)において温度 300～650℃、圧力 7～35 MPa で原料である炭素資源を亜臨界或いは超臨界水と反応させて前記炭素資源の熱分解又は加水分解のいずれか一方又は双方を行うことにより軽質化されたガス、油分及び残渣を生成し、

前記反応器(10)の第 2 反応領域(12)において温度 650～1200℃、圧力 7～35 MPa で前記軽質化されたガス、油分及び残渣を亜臨界或いは超臨界水と反応させて更に軽質化及びガス化することにより、水素、二酸化炭素、一酸化炭素及びメタンを主成分とするガスを生成し、

前記反応器(10)の第 3 反応領域(13)において温度 450～1000℃、圧力 7～35 MPa で前記ガスを水素及び二酸化炭素を主成分とするガスに転換する水素ガス等の製造方法であって、

前記第 2 反応領域(12)に酸化剤を添加してガス、油分、残渣の一部を燃焼させることにより前記第 1 及び第 2 反応領域(11,12)に必要な熱を補充するとともに前記第 3 反応領域(13)が前記第 1 反応領域(11)への熱交換及び吸熱反応により冷却されることを特徴とする水素ガス等の製造方法。

【請求項 2】 反応器(10)の第 1 反応領域(11)、第 2 反応領域(12)又は第 3 反応領域(13)のうち少なくとも 1 つの領域で添加剤を添加する請求項 1 記載の水素ガス等の製造方法。

【請求項 3】 第 3 反応領域(13)において転換した水素及び二酸化炭素を主成分とするガスを温度 20～31℃、圧力 2～35 MPa とすることにより、二酸化炭素を高純度の液体状態で回収する請求項 1 記載の水素ガス等の製造方法。

【請求項 4】 両端が封止された管状の反応器(10)の内周部に設けられた第 1 反応領域(11)と、前記反応器(10)の中心部に設けられた第 2 反応領域(12)と、前記反応器(10)の中心部に前記第 2 反応領域(12)に続いて設けられた第 3 反応領域(13)と、前記第 1、第 2 及び第 3 反応領域の圧力をいずれも 7～35 MPa に維持しかつ前記第 1、第 2 及び第 3 反応領域の温度をそれぞれ 300～650℃、650～1200℃及び 450～1000℃に維持する手段(22,27,32,25,28,33,16)とを有し、

前記反応器(10)の一端又は他端のいずれか一方又は双方に前記第 1 反応領域(11)に通じる炭素資源及び水の供給口(14a,14b,14c)が設けられ、

前記第 1 反応領域(11)と前記第 2 反応領域(12)とが筒状の熱良導体からなる耐熱性の仕切板(16)で区画され、前記仕切板(16)の反応器の他端側に前記第 1 反応領域(11)と前記第 2 反応領域(12)とを連通する連通部(17)を有し、

前記反応器(10)の他端に前記第 2 反応領域(12)に酸化剤

を供給する供給パイプ(18)が設けられ、

前記反応器(10)の一端に水素及び二酸化炭素を主成分とするガスの排出口(19)が設けられたことを特徴とする水素ガス等の製造装置。

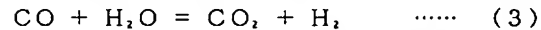
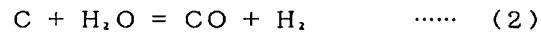
【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は重質油、石炭等の重質資源、又はこの重質資源を熱分解した炭素資源から清浄な水素ガスを製造する方法に関するものである。

【0002】

【従来の技術】一般に、炭素資源の炭素を水蒸気と反応させてガス化する場合、その反応は下記の反応式(1)～(3)で示される。



上記式(1)及び(2)では、反応が吸熱反応であるため、800～1800℃の高温で加熱することにより反応を促進し、また必要に応じて触媒を利用することにより炭素質を完全にガス化している。

【0003】

【発明が解決しようとする課題】しかしガス化炉で上記式(1)～(3)の反応により水素ガスを製造する場合、式(3)に基づく水性ガスシフト反応が十分に進行しないため、生成物中に未反応の一酸化炭素ガスが残留する。そのため、高価な触媒を使用したシフトコンバータを通し、式(3)の反応を進ませる必要がある。また原料の炭素資源には数%～十数%の灰分、金属不純物、硫黄、窒素等が含まれているため、これらを除くために生成物の精製を行う必要がある。また高温反応ではコーキング現象が生じて反応装置の一部が反応で生じたコークスにより閉塞され、反応装置に高価な耐熱材料が必要となる等の不都合がある。更に副産物である二酸化炭素ガスは回収が困難であるため、大気中に放出されており、環境上問題がある。

【0004】本発明の目的は、複雑なプロセスを要することなく、高純度の水素ガスを製造する方法及び装置を提供することにある。本発明の別の目的は、高純度の液化二酸化炭素を副産物として回収する方法及び装置を提供することにある。

【0005】

【課題を解決するための手段】請求項 1 に係る発明は、図 1 に示すように反応器 10 の第 1 反応領域 11 において温度 300～650℃、圧力 7～35 MPa で炭素資源を亜臨界或いは超臨界水と反応させてこの炭素資源の熱分解又は加水分解のいずれか一方又は双方を行うことにより軽質化されたガス、油分及び残渣を生成し、反応器 10 の第 2 反応領域 12 において温度 650～1200℃、圧力 7～35 MPa で上記軽質化されたガス、油分及び残渣を亜臨界或いは超臨界水と反応させて更に軽

質化及びガス化することにより、水素、二酸化炭素、一酸化炭素及びメタンを主成分とするガスを生成し、反応器10の第3反応領域13において温度450～1000℃、圧力7～35MPaで上記ガスを水素及び二酸化炭素を主成分とするガスに転換する水素ガス等の製造方法であって、第2反応領域12に酸化剤を添加してガス、油分、残渣の一部を燃焼させることにより上記第1、第2及び第3反応領域に必要な熱を補充するとともに第3反応領域が第1反応領域への熱交換及び吸熱反応により冷却されることを特徴とする水素ガス等の製造方法である。高圧の亜臨界或いは超臨界状態の水は流体密度が高いため、反応系内に存在する炭素資源の炭素粒子及び反応過程の活性種に対して効率良く接触する。従って、水素ガス及び二酸化炭素の生成条件を最適に設定しておくことにより高純度の水素ガス及び高純度の二酸化炭素が効率よく製造される。第1及び第2反応領域の反応の進行に必要な熱は、ガス、油分、残渣の一部を酸化剤により燃焼したときの燃焼熱によりに補充される。また第3反応領域の熱は第1反応領域の昇温に消費され、かつ第3反応領域の反応は吸熱反応であるため、第3反応領域の温度は第2反応領域の温度より低下する。

【0006】請求項2に係る発明は、請求項1に係る発明であって、反応器10の第1反応領域11、第2反応領域12又は第3反応領域13のうち少なくとも1つの領域で添加剤を添加する水素ガス等の製造方法である。アルカリ金属又はアルカリ土類金属の酸化物、水酸化物、炭酸塩等からなる添加剤を添加すると、上記式

(2)の水性ガス化反応と、上記式(3)の水性ガスシフト反応がより効率的に行われ、水素ガス及び二酸化炭素ガスを主成分とするガスがより多く生成される。

【0007】請求項3に係る発明は、請求項1に係る発明であって、第3反応領域13において転換した水素及び二酸化炭素を主成分とするガスを温度20～31℃、圧力2～35MPaとすることにより、二酸化炭素を高純度の液体状態で回収する水素ガス等の製造方法である。第3反応領域13において転換した水素及び二酸化炭素を主成分とするガスを温度及び圧力を操作することにより、水素と二酸化炭素を相分離させる。二酸化炭素を大気中に放出せずに液体状態で回収することにより、地球環境の温暖化防止につながるとともに、化学原料等へのリサイクルが可能になる。

【0008】請求項4に係る発明は、図1に示すように両端が封止された管状の反応器10の内周部に設けられた第1反応領域11と、反応器10の中心部に設けられた第2反応領域12と、反応器10の中心部に第2反応領域12に続いて設けられた第3反応領域13と、上記第1、第2及び第3領域の圧力をいずれも7～35MPaに維持しかつ上記第1、第2及び第3反応領域の温度をそれぞれ300～650℃、650～1200℃及び450～1000℃に維持する手段22、27、32、

25、28、33、16とを有し、反応器10の一端又は他端のいずれか一方又は双方に第1反応領域11に通じる炭素資源及び水の供給口14a、14b、14cが設けられ、第1反応領域11と第2反応領域12とが筒状の熱良導体からなる耐熱性の仕切板16で区画され、仕切板16の反応器10の他端側に第1反応領域11と第2反応領域12とを連通する連通部17を有し、反応器10の他端に第2反応領域12に酸化剤を供給する供給パイプ18が設けられ、反応器10の一端に水素及び二酸化炭素を主成分とするガスの排出口19が設けられたことを特徴とする水素ガス等の製造装置である。

【0009】酸化剤を加えて第2反応領域12を高温にして所望の反応を行わせると同時に、反応領域13で吸熱反応によるCOガスのシフト反応を行わせる。反応領域13で生じた余剰の熱を仕切板16を通して外部から供給される第1反応領域の原料等に吸収させ、これにより原料の熱分解・加水分解反応を行わせる。従って、第2反応領域12で燃焼が起れば、この熱が第1反応領域11の熱源となり、反応器外部からの熱エネルギーの供給を低減することができる。また高温の第2及び第3反応領域12、13を低温の第1反応領域11が仕切板を介して包囲するため、反応器10の周壁の熱的負荷が軽減され、反応器の周壁材料を選定する範囲が拡大する。本明細書において、「水の超臨界状態」又は「超臨界水」とは、374℃以上の温度で22MPa以上の圧力にある水の状態をいう。

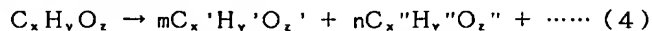
【0010】

【発明の実施の形態】本発明で原料として用いる炭素資源には、重質油（原油、A重油、B重油、C重油、常圧蒸留残渣、減圧蒸留残渣、ピチューメンなど）、超重質油、石炭（草炭、褐炭、亜瀝青炭、瀝青炭など）、石油コークス、石炭コークス、熱分解チャー、プラスチック、ゴム、天然ガス、石油ガス、メタンハイドレートなど、炭素を含む天然資源、廃材、廃棄物などが挙げられる。天然ガスなどのガスについては油分は発生しないが、他の固体ないし液体状の炭素資源と同様の処理による水素ガスの製造が可能である。また本発明の酸化剤には、酸素、空気又は過酸化水素等が挙げられる。更に本発明の添加剤には、カリウム、ナトリウム等のアルカリ金属の酸化物、水酸化物、炭酸塩等や、マグネシウム、カルシウム等のアルカリ土類金属の酸化物、水酸化物、炭酸塩等が挙げられる。

【0011】本発明では、図1に示すように、それぞれ圧力7～35MPaであって温度の異なる3つの反応領域11、12及び13を有する単一の反応器10において原料が処理される。この反応器10は両端が封止された管状に形成される。反応器10の外周部には保温のためのヒータ10aが、また内周部には第1反応領域11がそれぞれ設けられる。また反応器10の中心部には第2反応領域12が設けられ、この第2反応領域12に続

いて反応器10の中心部に第3反応領域13が設けられる。反応器10の一端には第1反応領域11に通じる炭素資源の供給口14a及び水の供給口14cがそれぞれ設けられ、反応器10の他端には第1反応領域11に通じる炭素資源の供給口14bが設けられる。第1反応領域11と第2反応領域12とは筒状の熱良導体からなる耐熱金属、例えばNi-Crの耐熱合金（商品名：MCアロイ、三菱マテリアル製）の仕切板16で区画される。仕切板16は反応器10の一端の内壁に密着し、反応器10の他端の内壁とは間隔をあけて設けられる。この間隔は第1反応領域11と第2反応領域12とを連通する連通部17を構成し、この部分から、熱分解などを受けた流体が反応領域12に流入する。この仕切板16は高温にさらされ、腐食が大きくなるおそれがあるため、仕切板16は交換可能に構成される。更に反応器11の他端の中心部には酸化剤の供給パイプ18が貫通し、仕切板16の端部から僅かに仕切板内部に入った第2反応領域12まで延びて設けられる。反応器10の一端には第3反応領域13で転換した水素及び二酸化炭素及び亜臨界水又は超臨界水からなる流体を排出する排出口19が設けられる。図1では単一の仕切板16を有する反応器10を示したが、仕切板の数はこれに限らず、例えば図3に示すように3重の仕切板16a、16b、16cで第2及び第3反応領域を包囲してもよい。この仕切板は2重、4重、5重でもよい。この仕切板の包囲数は、反応器10の外壁温度を十分に下げ、かつ原料を十分に熱分解させるに必要な数だけ設定する。即ち、この仕切板の包囲数は、熱回収率、原料の分解し易さ、仕切板の熱伝導性などから決定される。また図1及び図3では、分解生成したガスの排出口19を上部に、酸化剤の供給パイプ18を下部に有する反応器10を示しているが、反応器の設置方向はこの方向に限らず、排出口を下部に、供給パイプを上部にしてもよく、或いは反応器を水平方向に設置して排出口及び供給パイプを左右両側に配置するようにしてもよい。

【0012】炭素資源の供給口14a及び14bには、タンク21に貯えられた液状の原料がポンプ22で圧送されて予熱器25を介して供給される。タンク21の周囲にはヒータ24が設けられ、原料を100～200℃に加熱する。水の供給口14cには、タンク26に貯えられた水がポンプ27で圧送され、予熱器28で200～400℃に加熱されて供給される。供給パイプ18には、タンク31に貯えられた酸化剤である濃度50～6＊



但し、 $x > x' > x''$ 、 $y > y' > y''$ 、 $z > z' > z''$ であり、 m 、 n は任意数である。第1反応領域11では、上記式(4)の炭素資源の軽質化反応を行わせる以外に、第1反応領域の温度を600～800℃の高温側に変化させることにより、クラッキングによる水素生成や、残渣のガス化反応による水素生成を行わせることもでき

＊0%の過酸化水素水がポンプ32で圧送され、予熱器33で200～600℃に加熱されて供給される。タンク21にはアルカリ金属又はアルカリ土類金属の酸化物、水酸化物、炭酸塩等からなる添加剤が添加されることが好ましい。ポンプ22、27、32、予熱器25、28、33、仕切板16、ヒータ24、反応器10のヒータ10a及び第2反応領域12での燃焼により、反応器10の内部が300～1200℃に維持される。排出口19には分離器40が接続され、ここで各種ガスが分離される。この実施の形態では分離器40はそれぞれ気液分離機能を有する第1分離器41及び第2分離器42により構成される。即ち、排出口19には冷却器43、第1分離器41及び減圧弁44が接続される。第1分離器41には更に冷却器46、第2分離器42及び減圧弁47が接続される。

【0013】次にこのような装置による反応について説明する。

(a) 第1反応領域での反応

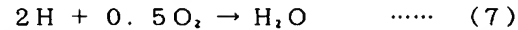
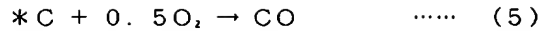
先ず原料の炭素資源と水を反応器10の第1反応領域11に導入し、温度300～650℃、圧力7～35MPaの水の亜臨界或いは超臨界状態で反応させる。この反応は炭素資源の熱分解又は加水分解のいずれか一方又は双方であり、この分解反応により軽質化されたガス、油分及び残渣が生成される。第1反応領域11の好ましい反応条件は、例えば原料が亜瀝青炭である場合、380～500℃、圧力10～30MPa程度であり、原料が瀝青炭である場合、480～650℃、圧力10～30MPa程度であり、原料が重質油の場合、400～600℃、圧力10～30MPa程度である。これらの条件は原料種類によって異なるため、最適な反応条件は、原料の種類に応じて決める必要がある。第1反応領域11の温度が300℃未満、圧力が7MPa未満では、反応速度が遅く、また第1反応領域11の温度が650℃を超え、圧力が35MPaを超えると、反応器10に負荷がかかり過ぎ、効率的でない。

【0014】炭素資源の熱分解・加水分解に際して、流動性を持たせるために、炭素資源が固体である場合には、炭素資源を水と混合してスラリーの形態で第1反応領域11に供給する。これにより反応が促進され、コーキング現象が抑制される。炭素資源は第1反応領域11内で熱分解及び加水分解により次の反応式(4)に示すように軽質化される。

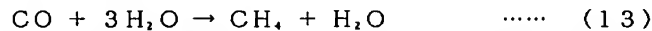
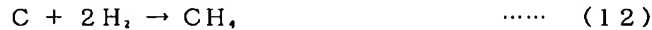
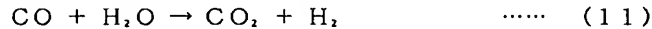
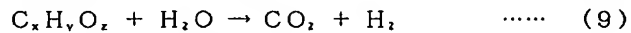
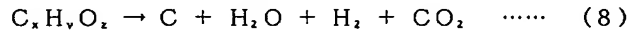
【0015】(b) 第2反応領域での反応

第1反応領域11で生成された軽質化されたガス、油分及び残渣が連通部17を通過して第2反応領域12に流入する。ここで酸化剤の過酸化水素水が供給パイプ18により第2反応領域12に供給される。この酸化剤にはア

ルカリ金属又はアルカリ土類金属の酸化物、水酸化物、炭酸塩等からなる添加剤を添加してもよい。酸化剤と流入してきたガス、油分及び残渣の一部が燃焼し、燃焼熱により第2反応領域12が650～1200℃の高温になる。この燃焼反応は、次の式(5)～(7)で示される。



燃焼反応以外の第2反応領域12における反応は次の反応式(8)～(13)で示される。



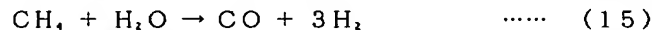
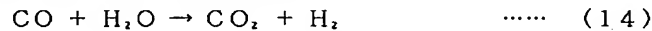
上記反応により軽質化されたガス、油分及び残渣は更に軽質化及びガス化され、水素、二酸化炭素、一酸化炭素及びメタンを主成分とするガスが生成される。第2反応領域12の好ましい温度は700～1100℃であり、好ましい圧力は10～30MPaである。

【0016】(c) 第3反応領域での反応

第2反応領域12で生成された水素、二酸化炭素、一酸化炭素及びメタンを主成分とするガスは、第3反応領域※20

※13において水素及び二酸化炭素を主成分とするガスに転換する。この第3反応領域13の温度は450～1000℃、圧力は7～35MPaである。第3反応領域13の好ましい温度は550～800℃であり、好ましい圧力は10～30MPaである。第3反応領域13における反応は次の反応式(14)～(15)で示される。

【0017】



本発明では上記第3反応領域13での転換反応に基づいて、水素及び二酸化炭素を主成分とするガスを製造することを主目的としている。しかしその他にも、反応温度、反応圧力、添加剤等を適宜組合わせることにより上記反応式(8)～(15)に基づいて一酸化炭素ガス又はメタンガスに富んだガスを製造することも可能である。図2(a)に水素ガス及び液化二酸化炭素を製造するときのブロック図を示す。高温高圧下では、生成した水素及び二酸化炭素は亜臨界或いは超臨界水と均一相となるが、圧力及び温度を下げていくと、水素ガスと液化二酸化炭素を個別に分離することができる。図2(b)に水素ガス、一酸化炭素ガス及び液化二酸化炭素を製造するときのブロック図を示す。図2(c)に水素ガス、メタンガス及び液化二酸化炭素を製造するときのブロック図を示す。図2(a)～(c)において、図1と同一符号は図1と同一機器を示す。

【0018】これらの各成分を水の亜臨界或いは超臨界状態から分離する方法について説明する。反応器10内部の温度、圧力で水は亜臨界或いは超臨界状態となり、水素、二酸化炭素、一酸化炭素及びメタンも超臨界状態にある。それぞれの超臨界点は、次の表1に示される。

【0019】

【表1】

ガスの成分	温度(℃)	圧力(MPa)
水	374	22.4
二酸化炭素	31	7.5
水素	-240	1.3
一酸化炭素	-140	3.5
メタン	-82.7	4.7

【0020】水、二酸化炭素、水素、一酸化炭素及びメタンを含む混合ガスの温度及び圧力を水の超臨界点以下でかつ二酸化炭素の超臨界点以上にする、上記表1より明らかなように、水のみが超臨界相から液体として、密度がほぼ1g/cm³の水として相分離する。次に水が分離された超臨界流体の圧力と温度を制御し、二酸化炭素の超臨界点以下で水素、メタンの超臨界点以上にする。好ましくは20℃で5MPa程度に冷却、減圧することにより、二酸化炭素を液化させ、相分離させる。引続いて水分離と同じ方法で液化二酸化炭素のみを分離することによりメタン、水素、一酸化炭素が得られる。図2(a)、(b)及び(c)のいずれの方法でも、上記操作で所望の成分を分離することができる。液化二酸化炭素への他のガス成分の溶解度は小さいため、純度の高い液化二酸化炭素が得られる。

【0021】図1に戻って、第3反応領域13で転換した水素及び二酸化炭素を主成分とするガスは反応器10

の排出口19から冷却器43で水の超臨界点以下の温度まで冷却される。冷却されたガスは分離器41内で気液に分離させ液体の水のみを減圧弁44を通して抜き出す。これにより水のみが液体として分離される。残りの気体は冷却器46に送られ、ここで20℃まで冷却された後、分離器42内で液体CO₂と気体に分離させる。気体は水素ガスを主成分とするガスであり、液体の二酸化炭素が減圧弁47を通して抜き出される。

【0022】

【実施例】次に本発明の実施例を説明する。

<実施例1>石炭を窒素雰囲気中800℃で乾留したものを炭素資源として用いて水素及び二酸化炭素を含むガスの製造を試料1～試料6について行った。6種類の試料において、反応器内の圧力を25MPaとし、第2反応領域の温度が650℃、800℃及び1000℃となるように酸化剤の過酸化水素を供給した。また酸化剤の*

*みによる発熱では熱量が不十分なため、反応器を外側から加熱した。試料2、試料4及び試料6では添加剤として炭酸カリウムを使用した。未反応物は反応器内に蓄積しており、これを残渣として回収した。反応器の排出口から得られた生成物は、図1に示した分離器では分離せずに、図示しないガス凝縮器で凝縮し、流量計でガス量を測定した後、生成ガスを容器に一時貯蔵した。この容器に貯えられたガスをサンプリングして成分を分析した。その結果を表2に示す。表2より明らかなように、試料1～6はいずれも多量の水素ガスと二酸化炭素ガスが得られることが判った。特に添加剤を加えた場合には一酸化炭素とメタンの生成が抑制される傾向が確認された。また第2反応領域の温度を1200℃の条件としたときも同じ傾向が確認された。

【0023】

【表2】

試料No	温度-圧力-触媒	ガス成分(容積%)			
		H ₂	CO ₂	CO	CH ₄
試料1	650℃-25MPa	63	34	0	3
試料2	650℃-25MPa-K ₂ CO ₃	66	34	0	0
試料3	800℃-25MPa	52	37	3	9
試料4	800℃-25MPa-K ₂ CO ₃	65	34	0	1
試料5	1000℃-25MPa	51	26	8	15
試料6	1000℃-25MPa-K ₂ CO ₃	62	35	1	2

【0024】<実施例2>石油蒸留残渣を炭素資源として用いた以外は実施例1と同様の方法を繰返して水素及び二酸化炭素を含むガスの製造を試料7～試料12について行った。その結果を表3に示す。表3より明らかなように、本発明の試料7～12はいずれも多量の水素ガスと二酸化炭素ガスが得られることが判った。特に添加※

30※剤を加えた場合には一酸化炭素が抑制される傾向が確認された。また第2反応領域の温度を1200℃の条件としたときも同じ傾向が確認された。

【0025】

【表3】

試料No	温度-圧力-触媒	ガス成分(容積%)			
		H ₂	CO ₂	CO	CH ₄
試料7	650℃-25MPa	45	25	0	30
試料8	650℃-25MPa-K ₂ CO ₃	61	23	0	16
試料9	800℃-25MPa	46	24	4	26
試料10	800℃-25MPa-K ₂ CO ₃	67	25	0	7
試料11	1000℃-25MPa	55	26	8	11
試料12	1000℃-25MPa-K ₂ CO ₃	66	30	1	3

【0026】<実施例3>第2反応領域の温度を800 50℃とし、添加剤の種類を変化させた以外は実施例1と同

様の方法を繰返して水素及び二酸化炭素を含むガスの製造を試料13～試料20について行った。その結果を表4に示す。表4より明らかなように、試料13～20はいずれも多量の水素ガスと二酸化炭素ガスが得られることが判った。特に添加剤を加えた場合には一酸化炭素と*

*メタンの生成が抑制される傾向が確認された。またガスの生成速度はアルカリ金属塩がアルカリ土類塩より大きくなる傾向を示した。

【0027】

【表4】

試料No	温度-圧力-触媒	ガス成分 (容積%)			
		H ₂	CO ₂	CO	CH ₄
試料13	800℃-25MPa	52	37	3	9
試料14	800℃-25MPa-K ₂ CO ₃	65	34	0	1
試料15	800℃-25MPa-KOH	63	35	1	1
試料16	800℃-25MPa-Na ₂ CO ₃	65	35	1	1
試料17	800℃-25MPa-NaOH	65	34	1	2
試料18	800℃-25MPa-CaCO ₃	66	34	0	1
試料19	800℃-25MPa-Ca(OH) ₂	62	35	1	2
試料20	800℃-25MPa-MgCO ₃	62	34	1	3

【0028】<実施例4>反応器内の圧力を7、10、25MPaとし、第2反応領域の温度を800℃とした以外は実施例1と同様の方法を繰返して水素及び二酸化炭素を含むガスの製造を試料21～試料23について行った。その結果を表5に示す。なお、試料21～試料2※

※3については添加剤を加えていない。表5より明らかなように、試料21～23はいずれも多量の水素ガスと二酸化炭素ガスが得られることが判った。

【0029】

【表5】

試料No	温度-圧力-触媒	ガス成分 (容積%)			
		H ₂	CO ₂	CO	CH ₄
試料21	800℃-25MPa	52	37	3	9
試料22	800℃-10MPa	54	35	4	7
試料23	800℃-7MPa	55	35	4	6

【0030】<実施例5>ポリプロピレンを炭素資源として用いた以外は実施例1と同様の方法を繰返して水素及び二酸化炭素を含むガスの製造を試料24～試料26について行った。その結果を表6に示す。なお、試料24～試料26については添加剤を加えていない。表6より明らかなように、本発明の試料24～26はいずれも

多量の水素ガスと二酸化炭素ガスが得られることが判った。特に第2反応領域の温度を低く設定した場合は一酸化炭素が抑制され、メタンが多く生成される傾向が確認された。

【0031】

【表6】

試料No	温度-圧力-触媒	ガス成分(容積%)			
		H ₂	CO ₂	CO	CH ₄
試料24	650℃-25MPa	58	32	0	10
試料25	800℃-25MPa	59	32	2	7
試料26	1000℃-25MPa	61	30	6	3

【0032】

【発明の効果】以上述べたように、本発明によれば、反応器の第1反応領域において温度300～650℃、圧力7～35MPaで炭素資源を亜臨界或いは超臨界水と反応させて一次分解することにより軽質化されたガス、油分及び残渣を生成し、第2反応領域において温度650～1200℃、圧力7～35MPaで上記軽質化されたガス、油分及び残渣を亜臨界或いは超臨界水と反応させて更に軽質化及びガス化することにより、水素、二酸化炭素、一酸化炭素及びメタンを主成分とするガスを生成し、第3反応領域において温度450～1000℃、圧力7～35MPaで上記ガスを水素及び二酸化炭素を主成分とするガスに転換し、第2反応領域に酸化剤を添加してガス、油分、残渣の一部を燃焼させることにより上記第1及び第2反応領域に必要な熱を補充するとともに第3反応領域が第1反応領域への熱交換及び吸熱反応により冷却されるようにしたので、複雑なプロセスを要することなく、高純度の水素ガスを製造することができる。また超臨界点の差異を利用して分離器により高純度*

10*の液化二酸化炭素を副産物として回収することができる。

【図面の簡単な説明】

【図1】本発明の水素ガス等の製造装置の構成図。

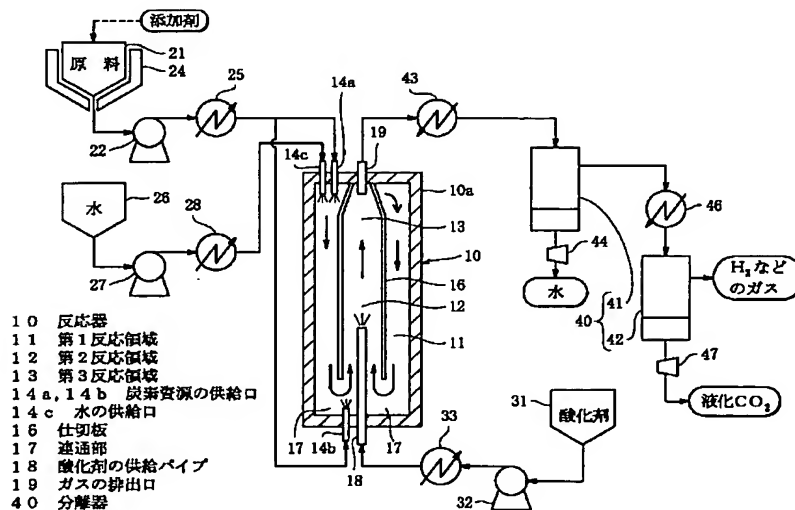
【図2】本発明の水素ガスと二酸化炭素その他の製造を示すブロック図。

【図3】本発明の別の反応器の構成図。

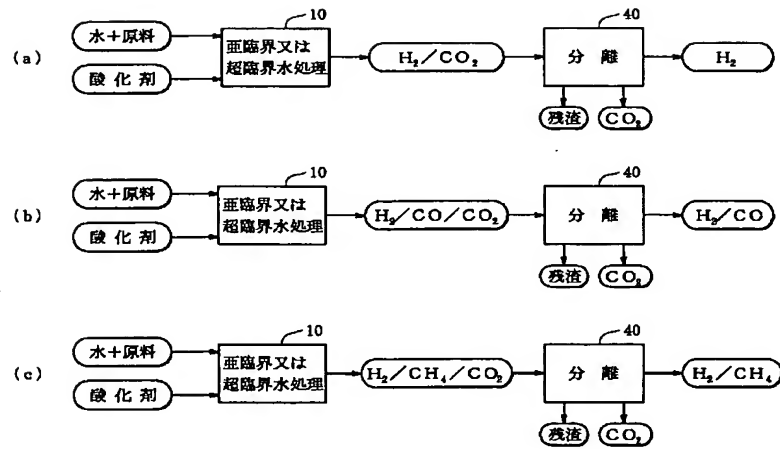
【符号の説明】

- 10 反応器
- 11 第1反応領域
- 12 第2反応領域
- 13 第3反応領域
- 14a, 14b 炭素資源の供給口
- 14c 水の供給口
- 16 仕切板
- 17 連通部
- 18 酸化剤の供給パイプ
- 19 ガスの排出口

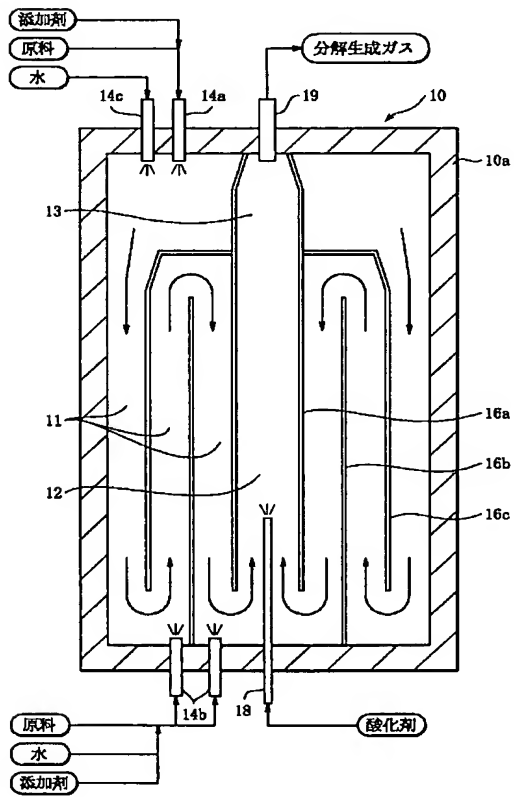
【図1】



【図2】



【図3】



フロントページの続き

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